CHAPTER 4

D & f Block Elements

CLASS 12TH

NCERT EXERCISE AND SOLUTIONS - CHEMISTRY

Q. 1. Write down the electronic configuration of:

(i)	**Cr^{3+}**	(ii)	**Pm^{3+}**	(iii)	**Cu^{+}**	(iv)	**Ce^{4+}**
(v)	**Co^{2+}**	(vi)	**Lu^{2+}**	(vii)	**Mn^{2+}**	(viii)	**Th^{4+}**

ANSWER:-

Here are the correct electronic configurations:

(i) Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3 \rightarrow [Ar]\ 3d^3$

(ii) Pm^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^4 \rightarrow [Xe]\ 4f^4$

(iii) Cu^{+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10} \rightarrow [Ar]\ 3d^{10}$

(iv) Ce^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6 \rightarrow [Xe]\ 4f^0 5d^0 6s^0$

(v) Co^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7 \rightarrow [Ar]\ 3d^7$

(vi) Lu^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14} \rightarrow [Xe]\ 4f^{14}$

(vii) Mn^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5 \rightarrow [Ar]\ 3d^5$

(viii) Th^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6 \rightarrow [Rn]5f^0 6d^0 7s^0$

Q. 2. Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

ANSWER:-

The electronic configuration of Mn^{2+} is $[Ar]\ 3d^5$, while that of Fe^{2+} is $[Ar]\ 3d^6$. It is well known that half-filled and fully filled orbitals provide extra stability. As a result, Mn^{2+}, with its stable d^5 configuration, resists oxidation to Mn^{3+}. On the other hand, Fe^{2+} has a $3d^6$ configuration, and by losing one electron, it attains the more stable $3d^5$ configuration. This makes Fe^{2+} more prone to oxidation to the Fe^{3+} state.

Q. 3. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

ANSWER:-

The oxidation states exhibited by the first half of the first-row transition metals are

Element	Sc	Ti	V	Cr	Mn
Oxidation States		+2	+2	+2	+2

	+3	+3	+3	+3	+3
		+4	+4	+4	+4
		+5	+5	+6	
			+6	+7	

It is evident that, except for Scandium (Sc), all these metals exhibit a +2 oxidation state. As we move from Sc to Mn, the atomic number increases from 21 to 25, meaning the number of electrons in the 3d orbital also increases from 1 to 5 in the +2 oxidation state.

Ion	Electronic Configuration
Sc^{2+}	$[Ar]\ 3d^1$
Ti^{2+}	$[Ar]\ 3d^2$
V^{2+}	$[Ar]\ 3d^3$
Cr^{2+}	$[Ar]\ 3d^4$
Mn^{2+}	$[Ar]\ 3d^5$

The +2 oxidation state is achieved by the loss of two 4s electrons in these metals. As the number of d electrons in the +2 oxidation state increases from Ti^{2+} to Mn^{2+}, the stability of the +2 state also increases. This is because the d-orbital progressively approaches a half-filled configuration, which is energetically favorable. Mn^{2+} ($3d^5$) has a half-filled d-subshell, making it highly stable.

Q. 4. **To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.**

ANSWER:-

The elements in the first half of the transition series exhibit multiple oxidation states, with Mn displaying the maximum number of oxidation states (+2 to +7). The stability of the +2 oxidation state increases as the atomic number rises due to the progressive filling of d-orbitals.

However, Scandium (Sc) does not exhibit a +2 oxidation state. Its electronic configuration is $[Ar]\ 4s^2\ 3d^1$, and it loses all three valence electrons to form Sc^{3+}. The +3 oxidation state of Sc is highly stable because it attains a noble gas configuration ([Ar]) upon electron loss. Similarly, Ti^{4+} and V^{5+} are also very stable for the same reason.

For Manganese (Mn), the +2 oxidation state is particularly stable because losing two electrons results in a half-filled $3d^5$ configuration ($[Ar]\ 3d^5$), which is energetically favorable.

Q. 5. **What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms : $3d^3$, $3d^5$, $3d^8$ and $3d^4$?**

ANSWER:-

The stable oxidation states of transition elements can be predicted based on their d-electron configurations in their ground state.

d-Electron Configuration	Possible Element	Stable Oxidation State	Reason
$3d^3$	Vanadium (V)	+2, +3, +4, +5	V^{5+} ([Ar]) is stable, but V^{3+} ([Ar] $3d^2$) is also common.
$3d^5$	Manganese (Mn)	+2, +4, +7	Mn^{2+} ([Ar] $3d^5$) is very stable due to half-filled d-subshell. Mn^{7+} (MnO_4^-) is also common.
$3d^8$	Cobalt (Co) or Nickel (Ni)	+2, +3	Co^{2+} ([Ar] $3d^7$) and Ni^{2+} ([Ar] $3d^8$) are stable oxidation states.
$3d^4$	Chromium (Cr)	+2, +3, +6	Cr^{3+} ([Ar] $3d^3$) is highly stable. Cr^{6+} (as in CrO_4^{2-}) is also common.

Thus, the most stable oxidation states are:

- $3d^3 \rightarrow +3$ (Vanadium, V^{3+})
- $3d^5 \rightarrow +2$ (Manganese, Mn^{2+}, due to half-filled stability)
- $3d^8 \rightarrow +2$ (Nickel or Cobalt, Ni^{2+} or Co^{2+})
- $3d^4 \rightarrow +3$ (Chromium, Cr^{3+}, stable d^3 configuration)

Q. 6. Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

ANSWER:-

(i) Vanadate, VO_3^- Oxidation state of V is + 5.

(ii) Chromate, CrO_4^{2-} Oxidation state of Cr is + 6.

(iii) Permanganate, MnO_4^- Oxidation state of Mn is + 7.

Q. 7. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

ANSWER:-

As we progress through the lanthanoid series, the atomic number increases gradually by one, meaning that both the number of protons and electrons in the atom also increase by one. Since electrons are being added to the same shell (4f orbital), the effective nuclear charge increases.

This occurs because the increase in nuclear attraction due to the addition of protons is more significant than the increase in interelectronic repulsions caused by the added electrons. Additionally, as the atomic number rises, the number of 4f electrons also increases. However, 4f electrons exhibit poor shielding, leading to a greater effective nuclear charge experienced by the outer electrons. As a result, the nucleus attracts the outermost electrons more strongly, causing a gradual decrease in the atomic size of lanthanoids. This phenomenon is known as lanthanoid contraction.

Consequences of Lanthanoid Contraction

1. Similarity in properties between the second and third transition series.
2. Facilitates the separation of lanthanoids due to small size differences.
3. Variation in the basic strength of lanthanide hydroxides—the basicity decreases from $La(OH)_3$ to $Lu(OH)_3$.

Q. 8. **What are the characteristics of the transition elements and why are they called transition elements? Which of the d-block** elements may not be regarded as the transition elements?

ANSWER:-

Transition elements are those elements whose atoms or stable ions possess a partially filled d-orbital. These elements belong to the d-block and exhibit properties that transition between the s-block and p-block, hence the name transition elements.

However, elements like Zn, Cd, and Hg are not considered transition elements because they have a completely filled d-subshell in both their atomic and common oxidation states.

Q. 9. **In what way is the electronic configuration of the transition elements different from that of the non-transition elements?**

ANSWER:-

Transition metals have a partially filled d-orbital, and their general electronic configuration is $(n-1)d^{1-10}\,ns^{0-2}$.

In contrast, non-transition elements either lack a d-orbital or have a completely filled d-orbital. Their general electronic configuration follows ns^{1-2} for s-block elements and $ns^2\,np^{1-6}$ for p-block elements.

Q. 10. **What are the different oxidation states exhibited by the lanthanoids?**

ANSWER:-

In the lanthanide series, the +3 oxidation state is the most prevalent, making Ln(III) compounds the dominant form. However, +2 and +4 oxidation states can also occur, either in solution or in solid compounds.

Q. 11. **Explain giving reasons:**

(i) **Transition metals and many of their compounds show paramagnetic behaviour.**
(ii) **The enthalpies of atomisation of the transition metals are high.**
(iii) **The transition metals generally form coloured compounds.**
(iv) **Transition metals and their many compounds act as good catalyst.**

ANSWER:-

(i) Transition metals exhibit paramagnetic behavior due to the presence of unpaired electrons, each of which possesses a magnetic moment associated with its spin angular momentum and orbital angular momentum. However, in the first transition series, orbital angular momentum is quenched, meaning that the observed paramagnetism is solely due to the unpaired electrons.

(ii) Transition elements possess a high effective nuclear charge and a large number of valence electrons, leading to the formation of strong metallic bonds. Consequently, they have a high enthalpy of atomization.

(iii) Most transition metal complexes are coloured due to the absorption of visible light, which promotes an electron transition between d-orbitals. In the presence of ligands, the d-orbitals split into two energy levels. Electrons can transition between these levels, requiring energy that corresponds to the visible light region. As a result, transition metal ions absorb light of a specific wavelength, while the remaining wavelengths are reflected, giving the solution its characteristic colour.

(iv) The catalytic activity of transition elements is due to:

- **(a)** Their ability to exhibit variable oxidation states and form unstable intermediates, lowering the activation energy (E_a).
- **(b)** Providing a suitable surface for reactions to occur efficiently.

Q. 12. **What are interstitial compounds? Why are such compounds well known for transition metals?**

ANSWER:-

Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds.

Q. 13. **How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.**

ANSWER:-

In transition elements, the oxidation state can range from +1 to the maximum possible state by losing all valence electrons. Additionally, their oxidation states typically differ by 1 (e.g., Fe^{2+}/Fe^{3+}, Cu^{+}/Cu^{2+}). In contrast, non-transition elements usually exhibit oxidation states differing by 2 (e.g., +2 and +4, or +3 and +5).

Q. 14. **Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?**

ANSWER:-

Potassium dichromate is prepared from chromite ore ($FeCr_2O_4$) in the following steps.

Step 1: Preparation of sodium chromate

$$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

Step 2: Conversion of sodium chromate into sodium dichromate

$$2Na_2CrO_4 + \text{ conc. } H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Step 3: Conversion of sodium dichromate to potassium dichromate

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Potassium dichromate being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration. The dichromate ion $\left(Cr_2O_7^{2-}\right)$ exists in equilibrium with chromate $\left(CrO_4^{2-}\right)$ ion at pH4. However, by changing the pH, they can be interconverted.

$$2CrO_4^{2-} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} 2HCrO_4^- \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} Cr_2O_7^{2-}$$

Q.15. **Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:**

(i) **iodide** **(ii)** **iron(II) solution and** **(iii)** **H_2S**

ANSWER:-

$K_2Cr_2O_7$ acts as a very strong oxidising agent in the acidic medium.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$K_2Cr_2O_7$ takes up electrons to get reduced and acts as an oxidising agent. The reaction of $K_2Cr_2O_7$ with other iodide, iron (II) solution, and H_2S are given below.

(i) $K_2Cr_2O_7$ oxidizes iodide to iodine.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\left. 2I^- \rightarrow I_2 + 2e^- \right] \times 3$$
$$\overline{\underline{Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O}}$$

(ii) $K_2Cr_2O_7$ oxidizes iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\left. Fe^{2+} \rightarrow Fe^{3+} + e^- \right] \times 6$$
$$\overline{\underline{Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}}$$

(iii) $K_2Cr_2O_7$ oxidizes H_2S to sulphur.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\left. H_2S \rightarrow S + 2H^+ + 2e^- \right] \times 3$$
$$\overline{\underline{Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O}}$$

Q. 16. **Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with**

(i) **iron(II) ions**

(ii) **SO_2 and**

(iii) **oxalic acid?**

Write the ionic equations for the reactions.

ANSWER:-

Potassium permanganate ($KMnO_4$) is prepared from pyrolusite (MnO_2) by fusing the ore with KOH in the presence of atmospheric oxygen or an oxidizing agent like KNO_3 or $KClO_4$, resulting in the formation of potassium manganate (K_2MnO_4).

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{heat}} \underset{\text{(Green)}}{2K_2MnO_4} + 2H_2O$$

The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution. Electrolytic oxidation

$$K_2MnO_4 \leftrightarrow 2K^+ + MnO_4^{2-}$$
$$H_2O \leftrightarrow H^+ + OH^-$$

At anode, manganate ions are oxidized to permanganate ions.

$$\underset{\text{Green}}{MnO_4^{2-}} \leftrightarrow \underset{\text{Purple}}{MnO_4^-} + e^-$$

Oxidation by chlorine

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$
$$2MnO_4^{2-} + Cl_2 \rightarrow 2MnO_4^- + 2Cl^-$$

Oxidation by ozone

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$$
$$2MnO_4^{2-} + O_3 + H_2O \rightarrow 2MnO_4^{2-} + 2OH^- + O_2$$

(i) Acidified $KMnO_4$ solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^- \Big] \times 5$$
$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(ii) Acidified potassium permanganate oxidizes SO_2 to sulphuric acid.

$$MnO_4^- + 6H^+ + 5e^- \rightarrow Mn^{2+} + 3H_2O \Big] \times 2$$
$$2H_2O + 2SO_2 + O_2 \rightarrow 4H^+ + 2SO_4^{2-} + 2e^- \Big] \times 5$$
$$2MnO_4^- + 10SO_2 + 5O_2 + 4H_2O \rightarrow 2Mn^{2+} + 10SO_4^{2-} + 8H^+$$

(iii) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \Big] \times 2$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \Big] \times 5$$
$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Q. 17. **For M^{2+}/M and M^{3+}/M^{2+} systems, the E^- values for some metals are as follows:**

Cr^{2+}/Cr −0.9V

Cr^{3+}/Cr^{2+} −0.4 V

Mn^{2+}/Mn −1.2V

Mn^{3+}/Mn^{2+} +1.5 V

Fe^{2+}/Fe −0.4V

Fe^{3+}/Fe^{2+} +0.8 V

Use this data to comment upon:

(i) The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} and

(ii) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

ANSWER:-

(i) The standard reduction potential (E°) for the Fe^{3+}/Fe^{2+} pair is higher than that of Cr^{3+}/Cr^{2+} but lower than that of Mn^{3+}/Mn^{2+}. This indicates that the reduction of Fe^{3+} to Fe^{2+} is easier compared to Mn^{3+} to Mn^{2+}, but more difficult than Cr^{3+} to Cr^{2+}. Consequently, Fe^{3+} is more stable than Mn^{3+}, but less stable than Cr^{3+}.

Thus, the stability order of these ions is:

$Mn^{3+} < Fe^{3+} < Cr^{3+}$

(ii) The reduction potential values follow the order:

$Mn^{2+}/Mn < Cr^{2+}/Cr < Fe^{2+}/Fe$

This suggests that Fe is the least likely to oxidize to Fe^{2+}, while Mn oxidizes most readily to Mn^{2+}. Hence, the order of increasing ease of oxidation is:

$Fe < Cr < Mn$

Q. 18. Predict which of the following will be coloured in aqueous solution? Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each.

ANSWER:-

Coloration of Transition Metal Ions

Only ions with partially filled d-orbitals, where d-d transitions are possible, exhibit color in aqueous solutions. Ions with empty or completely filled d-orbitals appear colorless as no d-d transitions can occur.

Electronic Configurations and Coloration

Element	Atomic Number	Ionic State	Electronic Configuration in Ionic State	Color in Aqueous Solution
Ti	22	Ti^{3+}	$[Ar]\ 3d^1$	Colored
V	23	V^{3+}	$[Ar]\ 3d^2$	Colored
Cu	29	Cu^{+}	$[Ar]\ 3d^{10}$	Colorless (Fully filled d-orbital)
Sc	21	Sc^{3+}	[Ar]	Colorless (Empty d-orbital)
Mn	25	Mn^{2+}	$[Ar]\ 3d^5$	Colored
Fe	26	Fe^{3+}	$[Ar]\ 3d^5$	Colored
Co	27	Co^{2+}	$[Ar]\ 3d^7$	Colored

From the table, Sc^{3+} (empty d-orbital) and Cu^{+} (fully filled d-orbital) are colorless, while all other ions exhibit color due to d-d transitions.

Q. 19. **Compare the stability of +2 oxidation state for the elements of the first transition series.**

ANSWER:-

Oxidation States of First-Row Transition Elements

The table below shows the oxidation states exhibited by the first-row transition metals. Manganese (Mn) exhibits the maximum number of oxidation states (+2 to +7). The number of oxidation states increases from Sc to Mn due to the increasing number of unpaired electrons. However, from Mn to Zn, the number of oxidation states decreases as fewer unpaired electrons are available for bonding.

Additionally, the +2 oxidation state becomes more stable as we move down the group because the removal of the third electron from the d-orbital becomes increasingly difficult.

Oxidation States of First-Row Transition Metals

Element	+1	+2	+3	+4	+5	+6	+7
Sc			+3				
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

This trend highlights the role of d-electron availability and stability of oxidation states in transition metals.

Q. 20. **Compare the chemistry of actinoids with that of the lanthanoids with special reference to:**

(i) **electronic configuration**

(ii) **atomic and ionic sizes and**

(iii) **oxidation state**

(iv) **chemical reactivity.**

ANSWER:-

Comparison of Lanthanoids and Actinoids

The table below highlights the key differences between lanthanoids and actinoids, focusing on their electronic configuration, oxidation states, atomic and ionic sizes, and chemical reactivity.

Property	Lanthanoids	Actinoids
Electronic Configuration	$[Xe]\ 4f^{0-14}\ 5d^{0-1}\ 6s^2$	$[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$
Nature of f-orbitals	4f orbitals are deeply buried and have less participation in bonding.	5f orbitals are more exposed and participate in bonding to a greater extent.

Oxidation States	Principal oxidation state: +3. Some elements show +2 and +4 due to extra stability of half-filled and fully filled orbitals.	Exhibit a wider range of oxidation states due to comparable energy levels of 5f, 6d, and 7s orbitals. However, +3 remains the most common oxidation state.
Atomic and Ionic Sizes	Exhibit lanthanoid contraction (gradual decrease in atomic and ionic radii).	Show actinoid contraction, which is more pronounced due to the poor shielding effect of 5f orbitals.
Chemical Reactivity	- Early lanthanoids are highly reactive, similar to calcium(Ca). - Reactivity decreases with increasing atomic number; later lanthanoids behave similarly to aluminum (Al).	- Highly reactive, especially in finely divided form. - React with boiling water to form a mixture of oxide and hydride. - React with most non-metals at moderate temperatures. - Resistant to alkalies, but slightly affected by nitric acid due to the formation of a protective oxide layer.

Q. 21. **How would you account for the following:**

(i) **Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.**

(ii) **Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.**

The d^1 configuration is very unstable in ions

ANSWER:-

(i) Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as t_{2g}^3 configuration, which is a more stable configuration. In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d-orbital and is highly stable.

(ii) Co(II) remains stable in aqueous solutions. However, in the presence of strong field ligands, it gets oxidized to Co(III). Despite the high third ionization energy of cobalt, the significant crystal field stabilization energy (CFSE) provided by strong field ligands compensates for this energy, making the oxidation favorable.

(iii) Ions with a d^1 configuration readily lose one more electron to attain a stable d^0 configuration. The high hydration or lattice energy is sufficient to remove the lone d-electron, making these ions strong reducing agents.

Q. 22. **What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.**

ANSWER:-

A relatively less stable oxidation state can sometimes undergo an oxidation-reduction reaction where it is simultaneously oxidized and reduced. This process is known as disproportionation.

E.g

(i) $3CrO_4^{3-} + 8H^+ \rightarrow 2CrO_4^{2-} + Cr^{3+} + 4H_2O$

Cr(V) Cr(VI) Cr(III)

(ii) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- \rightarrow MnO_2 + 2H_2O$

Mn(VI) Mn(VII) Mn(IV)

Q. 23. **Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?**

ANSWER:-

In the first transition series, Cu commonly exhibits a +1 oxidation state due to its stable electronic configuration, [Ar] $3d^{10}$. The fully filled d-orbital provides enhanced stability.

Q. 24. **Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+}, Cr^{3+}, V^{3+} and Ti^{3+}. Which one of these is the most stable in aqueous solution?**

ANSWER:-

Ion	Atomic Number	Electronic Configuration	Number of Unpaired Electrons	Stability in Aqueous Solution
Mn^{3+}	25	[Ar] $3d^4$	4	Less stable
Cr^{3+}	24	[Ar] $3d^3$	3	Most stable
V^{3+}	23	[Ar] $3d^2$	2	Moderate stability
Ti^{3+}	22	[Ar] $3d^1$	1	Least stable

Most Stable Ion in Aqueous Solution:

Cr^{3+} is the most stable in aqueous solutions because it has a half-filled t_{2g} configuration in an octahedral crystal field, leading to significant crystal field stabilization energy (CFSE).

Q. 25. **Give examples and suggest reasons for the following features of the transition metal chemistry:**

(i) **The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.**

(ii) **A transition metal exhibits highest oxidation state in oxides and fluorides.**

(iii) **The highest oxidation state is exhibited in oxoanions of a metal.**

ANSWER:-

(i) In lower oxides of transition metals, the metal is in a low oxidation state, meaning some valence electrons remain unbonded. This allows the oxide to donate electrons, making it basic in nature. In contrast, higher oxides have metals in high oxidation states, where most valence electrons are involved in bonding, leading to a higher effective nuclear charge. As a result, these oxides can accept electrons, making them acidic. For example: $Mn^{II}O$ is basic and $\overset{\text{vII}}{Mn}_2O_7$ is acidic.

(ii) Oxygen and fluorine are strong oxidizing agents due to their high electronegativity and small atomic size. As a result, they can induce the highest oxidation states in transition metals. Therefore, transition metals exhibit higher oxidation states in their oxides and fluorides. For example, in OsF_6 and V_2O_5, the oxidation states of Os and V are +6 and +5, respectively.

(iii) Oxygen is a strong oxidising agent due to its high electronegativity and small size. So, oxo-anions of a metal have the highest oxidation state. For example, in MnO_4^- the oxidation state of Mn is +7.

Q. 26. Indicate the steps in the preparation of:

(i) $K_2Cr_2O_7$ from chromite ore.

(ii) $KMnO_4$ from pyrolusite ore.

ANSWER:-

(i) Potassium dichromate ($K_2Cr_2O_7$) is prepared from chromite ore ($FeCr_2O_4$) in the following steps.

Step 1: Preparation of sodium chromate

$$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

Step 2: Conversion of sodium chromate into sodium dichromate

$$2Na_2CrO_4 + \text{ conc. } H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Step 3: Conversion of sodium dichromate to potassium dichromate

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration. The dichromate ion $\left(Cr_2O_7^{2-}\right)$ exists in equilibrium with chromate $\left(CrO_4^{2-}\right)$ ion at pH 4. However, by changing the pH, they can be interconverted.

$$2CrO_4^{2-} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} 2HCrO_4^- \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} Cr_2O_7^{2-}$$

Chromate Hydrogen Dichromate

(Yellow) (Chromate) (Orange)

(ii) Potassium permanganate ($KMnO_4$) can be prepared from pyrolusite (MnO_2). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as KNO_3 or $KClO_4$, to give K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{heat}} \underset{\text{(Green)}}{2K_2MnO_4} + 2H_2O$$

The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution. Electrolytic oxidation

$$K_2MnO_4 \rightarrow 2K^+ + MnO_4^{2-}$$

$$H_2O \rightarrow H^+ + OH^-$$

At anode, manganate ions are oxidized to permanganate ions.

$$MnO_4^{2-} \rightarrow MnO_4^- + e^-$$

Green Purple

Oxidation by chlorine

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$
$$2MnO_4^{2-} + Cl_2 \rightarrow 2MnO_4^- + 2Cl^-$$

Oxidation by ozone

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$$
$$2MnO_4^{2-} + O_3 + H_2O \rightarrow 2MnO_4^{2-} + 2OH^- + O_2$$

Q. 27. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

ANSWER:-

An alloy is a solid solution of two or more elements within a metallic matrix, forming either a partial or complete solid solution. Alloys generally exhibit distinct physical properties compared to their constituent elements. A notable lanthanoid alloy is Mischmetal, composed of 94−95% lanthanoids, 5% iron, and trace amounts of S, C, Si, Ca, and Al.

Uses of Mischmetal:

- Used in cigarette and gas lighters.
- Utilized in flame-throwing tanks.
- Applied in tracer bullets and shells.

Q. 28. What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.

ANSWER:-

Inner transition metals are elements in which the last electron enters the f-orbital. The elements with progressively filling 4f and 5f orbitals are known as f-block elements. Among the given atomic numbers, 59, 95, and 102 correspond to inner transition elements.

Q. 29. The chemistry of the actinoid elements is not so smooth as that of the Lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

ANSWER:-

Lanthanoids predominantly exhibit three oxidation states: +2, +3, and +4, with +3 being the most common. They have limited oxidation states due to the significant energy gap between 4f, 5d, and 6s orbitals. In contrast, actinoids display a wider range of oxidation states because the energy difference between 5f, 6d, and 7s orbitals is much smaller. For instance, uranium and plutonium show +3, +4, +5, and +6 oxidation states, while neptunium exhibits +3, +4, +5, and +7. Despite this variability, the +3 oxidation state remains the most prevalent in actinoids.

Q. 30. **Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.**

ANSWER:-

The last element in the actinoid series is lawrencium, Lr. Its atomic number is 103 and its electronic configuration is $[\mathrm{Rn}]5f^{14}6d^{1}7s^{2}$ .The most common oxidation state displayed by it is +3; because after losing 3 electrons it attains stable f14 configuration.

Q. 31. **Use Hund's rule to derive the electronic configuration of Ce3+ ion and calculate its magnetic moment on the basis of 'spin-only' formula.**

ANSWER:-

$\mathrm{Ce}: 1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}5s^{2}5p^{6}4f^{1}5d^{1}6s^{2}$

Magnetic moment can be calculated as: $\mu = \sqrt{n(n+2)}$ Where, n = number of unpaired electrons The electronic configuration of Ce^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^1$ In Ce^{3+}, n = 1

$\therefore\ \mu = \sqrt{1(1+2)} = \sqrt{3} = 1.732$ B.M

Q. 32. **Name the members of the lanthanoid series which exhibit +4 oxidation state and those which exhibit +2 oxidation state. Try to correlate this type of behavior with the electronic configurations of these elements.**

ANSWER:-

The lanthanides that exhibit +2 and +4 oxidation states are listed in the table below, with their atomic numbers in parentheses:

+2 Oxidation State	+4 Oxidation State
Nd (60)	Ce (58)
Sm (62)	Pr (59)
Eu (63)	Nd (60)
Tm (69)	Tb (65)
Yb (70)	Dy (66)

Ce^{4+} attains a stable [Xe] electronic configuration.

Tb^{4+} achieves stability with a half-filled [Xe] $4f^7$ configuration.

Eu^{2+} also attains a stable [Xe] $4f^7$ configuration.

Yb^{2+} becomes stable with a completely filled [Xe] $4f^{14}$ configuration.

Q. 33. **Compare the chemistry of the actinoids with that of lanthanoids with reference to:**

- (i) **electronic configuration**
- (ii) **oxidation states and**
- (iii) **chemical reactivity**

ANSWER:-

Comparison of Lanthanoids and Actinoids

Property	Lanthanoids	Actinoids
Electronic Configuration	[Xe] $4f^{0-14}$ $5d^{0-1}$ $6s^2$	[Rn] $5f^{1-14}$ $6d^{0-1}$ $7s^2$
Nature of f-Orbitals	4f orbitals are deeply buried and have minimal bonding involvement.	5f orbitals are less shielded and actively participate in bonding.
Oxidation States	Primarily +3, with occasional +2 and +4 states due to the stability of fully-filled and half-filled orbitals.	Exhibit a wider range of oxidation states due to similar energy levels of 5f, 6d, and 7s orbitals. The +3 state is most common.
Chemical Reactivity	Early lanthanoids are highly reactive, similar to Ca, but reactivity decreases with increasing atomic number, making them behave more like Al.	Actinoids are highly reactive, especially in finely divided form. They react with boiling water to form oxides and hydrides and readily combine with most non-metals. They are resistant to alkalis but slightly affected by nitric acid due to the formation of a protective oxide layer.

Q. 34. **Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.**

ANSWER:-

Atomic number	Electronic configuration
61	$[Xe]^{54} 4f^5 5d^0 6s^2$
91	$[Rn]^{86} 5f^2 6d^1 7s^2$
101	$[Rn]^{86} 5f^{13} 5d^0 7s^2$
109	$[Rn]^{86} 5f^{14} 6d^7 7s^2$

Q. 35. **Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:**

(i) **electronic configurations,**
(ii) **oxidation states,**
(iii) **ionisation enthalpies, and**
(iv) **atomic sizes.**

ANSWER:-

(i) In the 1st, 2nd, and 3rd transition series, the 3d, 4d, and 5d orbitals are progressively filled. Elements in the same vertical column typically exhibit similar electronic configurations. However, in the first transition series, there are two elements with anomalous electronic configurations.

$$\text{Cr}(24) = 3d^5 4s^1$$
$$\text{Cu}(29) = 3d^{10} 4s^1$$

Similarly, there are exceptions in the second transition series. These are

$Mo(42) = 4d^5 5s^1$

$\mathrm{Tc}(43) = 4d^6 5s^1$

$Ru(44) = 4d^7 5s^1$

$Rh(45) = 4d^8 5s^1$

$Pd(46) = 4d^{10} 5s^0$

$Ag(47) = 4d^{10} 5s^1$

There are some exceptions in the third transition series as well. These are:

$\mathrm{W}(74) = 5d^4 6s^2$

$Pt(78) = 5d^9 6s^1$

$\mathrm{Au}(79) = 5d^{10} 6s^1$

As a result of these exceptions, it happens many times that the electronic configurations of the elements present in the same group are dissimilar.

(ii) In all three transition series, the number of oxidation states is highest in the middle and lowest at the extremes. However, in the first transition series, the +2 and +3 oxidation states are generally stable for all elements. Most metals in this series form stable compounds in these oxidation states. In contrast, the stability of the +2 and +3 oxidation states decreases in the second and third transition series, where higher oxidation states become more significant. For example:

$$[\mathrm{Fe(CN)_6}]^{4-}, \left[\mathrm{Co}^{II'}(\mathrm{NH_3})_6\right]^{3+}, \left[\mathrm{Ti}(\mathrm{H_2O})_6\right]^{3+}$$

are stable complexes, but no such complexes are known for the second and third transition series such as Mo, W, Rh, In. They form complexes in which their oxidation states are high. For example: $\mathrm{WCl_6}$, $\mathrm{ReF_7}$, $\mathrm{RuO_4}$, etc.

(iii) In all three transition series, the first ionization enthalpy generally increases from left to right, with some exceptions. The third transition series has higher first ionization enthalpies than the first and second series due to the poor shielding effect of 4f electrons. Some elements in the second transition series have higher first ionization enthalpies than their counterparts in the first transition series, while others in the second series have lower ionization enthalpies than elements in the same vertical group of the first series.

(iv) Atomic size generally decreases across a period from left to right. In the second transition series, atomic sizes are larger than those of the corresponding elements in the first transition series. However, in the third transition series, atomic sizes are nearly the same as those in the second series due to lanthanoid contraction.

Q. 36. Write down the number of 3d electrons in each of the following ions:
$\mathrm{Ti^{2+}}$, $\mathrm{V^{2+}}$, $\mathrm{Cr^{3+}}$, $\mathrm{Mn^{2+}}$, $\mathrm{Fe^{2+}}$, $\mathrm{Fe^{2+}}$, $\mathrm{CO^{2+}}$, $\mathrm{Ni^{2+}}$ and $\mathrm{Cu^{2+}}$.
Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).

ANSWER:-

Here is the updated table including the number of d-electrons along with their filling in octahedral complexes:

Metal Ion	Number of d-Electrons	Filling of d-Orbitals (Octahedral Complex)
Ti^{2+}	2	t_{2g}^{2}
V^{2+}	3	t_{2g}^{3}
Cr^{3+}	3	t_{2g}^{3}
Mn^{2+}	5	$t_{2g}^{3} e_{g}^{2}$
Fe^{2+}	6	$t_{2g}^{4} e_{g}^{2}$
Fe^{3+}	5	$t_{2g}^{3} e_{g}^{2}$
Co^{2+}	7	$t_{2g}^{5} e_{g}^{2}$
Ni^{2+}	8	$t_{2g}^{6} e_{g}^{2}$
Cu^{2+}	9	$t_{2g}^{6} e_{g}^{3}$

Q. 37. **Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.**

ANSWER:-

The elements of the first transition series differ from heavier transition elements in several ways:

1. Atomic Size: First transition series elements are smaller than heavier ones. However, due to lanthanoid contraction, second and third series elements have similar sizes.
2. Oxidation States: +2 and +3 oxidation states are common in the first series, while heavier elements exhibit higher oxidation states more frequently.
3. Enthalpy of Atomisation: First transition series elements have lower enthalpies of atomisation than their heavier counterparts.
4. Melting & Boiling Points: Lower in the first series due to weaker metallic bonding compared to heavier elements.
5. Complex Formation: First-series elements form both low-spin and high-spin complexes, while heavier elements typically form only low-spin complexes.

Q. 38. **What can be inferred from the magnetic moment values of the following complex species?**

Example Magnetic	**Moment (BM)**
$K_4[Mn(CN)_6]$	**2.2**
$[Fe(H_2O)_6]^{2+}$	**5.3**
$K_2[MnCl_4]$	**5.9**

ANSWER:-

The magnetic moment (μ) is given by $\mu = \sqrt{n(n+2)}$, where n is the number of unpaired electrons:

- $K_4[Mn(CN)_6]$: $\mu = 2.2$ (closest to $n = 1$). Mn^{2+} (d^5) experiences strong field ligand (CN^-), leading to electron pairing.
- $[Fe(H_2O)_6]^{2+}$: $\mu = 5.3$ (closest to $n = 4$). Fe^{2+} (d^6) with weak field ligand (H_2O) does not cause electron pairing.
- $K_2[MnCl_4]$: $\mu = 5.9$ (closest to $n = 5$). Mn^{2+} (d^5) with weak field ligand (Cl^-) remains unpaired.